CHITOSAN AS A GREEN POLYMERIC INHIBITOR FOR MILD STEEL: ELECTROCHEMICAL BEHAVIOR IN SODIUM CHLORIDE MEDIUM

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Abstract – Some polymers have been indicated as effective corrosion inhibitors for different metals because they are able to form complexes with ions metal and on metal surfaces, blanketing the surface and protecting the metals from corrosive agents present in the solution. Chitosan and its derivatives are important materials having industrial and biological applications, and recently they are been considered as corrosion inhibitors for metals and alloys in various aggressive environments because of their green and environmental friendly nature. In this work, the inhibitive ability of water-soluble chitosan was examined by electrochemical potentiodynamic polarization (EPP) and impedance spectrometry (EIS) techniques. EPP and EIS studies showed that the corrosion potential (E_{corr}) becomes nobler and the charge transfer resistance increases with the concentration of chitosan. It was found that chitosan effectively hind carbon steel corrosion in acidic sodium chloride medium reaching inhibition efficiency above 70% for 800 ppm of the inhibitor.

Keywords: *Chitosan, green inhibitor, corrosion, mild steel.*

Introduction

Mild steel is the most common type of metal used in industries due to its acceptable properties and costs. However, as other oxidizable metals, it has low resistance to corrosion especially in alkaline and acid environments [1]. Corrosion control of metals is an important activity of technical, economical, environmental and aesthetic importance and the use of inhibitors is one of the best options of protecting metallic materials against corrosion [2]. Because of currently imposed environmental regulatory requirements for eco-friendly corrosion inhibitors, there is a growing interest in the use of natural products called of "green inhibitors" [3].

Green inhibitors include biocompatible, nontoxic, heavy metals free, eco-friendly polymers and natural substances. In recent years, there has been increased emphasis on applications of polymers, copolymers, grafted polymers, and polymer composites as green corrosion inhibitors. The good performance of a polymeric corrosion inhibitor is due to its larger size and greater number of functional anchoring groups. Through the anchoring groups, the polymers easily get adsorption on the metal surface and cover considerably more surface than the corresponding monomers. The main factors influencing the corrosion mitigating properties of the polymers are molecular size, weight, composition and nature of the anchoring groups. The solution pH, concentration, exposure time, and temperature also find their role in inhibition performance [4].

Natural polymers containing polar groups and heterocyclic compounds with polar groups and conjugated double bonds have been reported to inhibit carbon steel throughout their interaction with the metal surface via adsorption by the functional groups. The complexes formed with ions metal on metal surfaces blanket the surface and protect the metals from corrosive agents present in the solution. In general, the adsorption of the inhibitor depends on the nature and surface charge of the metal, the adsorption mode, its chemical structure and the type of electrolyte solution [5].

Chitosan is one of the most promising biodegradable polysaccharide produced from deacetylated of chitin that found naturally in the shells of shrimp and crab, well as fungi and cuticles of insets [6]. This natural polymer (Fig. 1) has structure consisting of N-glucosamine and N-acetyl-glucosamine units linked by β-1,4 glycoside. This polymer has been applied in many fields due its properties of biocompatibility, biodegradability, non-toxicity, antibacterial, antifungal and antitumor [7, 8]. The presence of oxygen and nitrogen heteroatoms in its structure qualifies chitosan, in part, as metals corrosion inhibitor. It has therefore been assessed for anticorrosive ability towards the corrosion of mild steel and copper in HCl environment [4, 9]. According to Fayomi [10], the chitosan corrosion ability is a function of its molecular structure, where its electron rich amino and hydroxyl groups are able to form bonding on the surface of the metals resulting in corrosion protection through coordinate bonding as these electrons are given out freely to the empty or partially occupied iron orbitals.
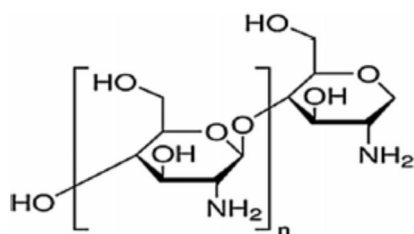

Figure 1- Molecular structure of chitosan [9]

This research aimed at examining the inhibitive ability of chitosan on the corrosion of carbon steel in diluted acid sodium chloride solution, employing electrochemical techniques of potentiodynamic polarization and impedance spectroscopy.

Experimental

Mild carbon steel AISI 1008 plates (composition in wt%: 0.0662 C, 0.3420 Mn, 0.0370 Al, 0.0260 Cr, 0.0160 P, 0.007 Si, 0.0010 Mo, rest Fe) were submitted to sanding (320, 600, 1200 and 2000# grit paper), alkaline degreasing (80ºC, 5 min), acid pickling (room temperature, 10 min) and drying under flow air stream.

Chitosan (from shrimp sheels) was commercially purchased and sodium chloride analytical grade from Anidrol were used without any further purification. Concentrations of 400 ppm and 800 ppm of chitosan added to in 0.1 M NaCl solution pH 3,5 ± 0.2 were employed in this study.

A Methrom DropSens 400*is* Potentiostat/Galvanostat connected to the Drop View software was used to perform electrochemical experiments at room temperature and under natural aired conditions. A platinum wire was used as counter electrode (CE), an Ag/AgCl electrode as reference electrode (RE) and the specimen as the working electrode (WE) with testing area of $1.0\ cm^2$. To gain the stable status of the working electrode it was immersed in aerated test solution for 30 min before each measurement, which allowed the open circuit potential (OCP) values to attain steady state. The potentiodynamic cathodic and anodic polarization curves were carried out by scanning from -500 mV to +500 mV

versus OCP at a scan rate of 5 mV/s. The linear Tafel segments of the anodic and cathodic curves were extrapolated to the corrosion potential (E_{corr}) to obtain the corrosion current densities (i_{corr}). Inhibition efficiency (η_{IE}) was calculated from i_{corr} values as shown in Eq. 1. All impedance measurements were carried out by using AC signals of amplitude 10 mV peak to peak at the steady state potential in the frequency range of 100 kHz to 10 mHz. The Nyquist pots were obtained from these measurements. EIS parameters from fitting of the equivalent circuit were used to calculate the inhibition efficiency by Eq. 2.

$$\eta_{IE}(\%) = \left(1 - \frac{i_{corr}\ (inhibitor)}{i_{corr}(uninhibitor)} \right) x\ 100 \quad (1)$$

$$\eta_{IE}(\%) = \left(1 - \frac{R_{ct}\ (uninhibito\ )}{R_{ct}\ (inhibitor)} \right) x\ 100 \quad (2)$$

Results and Discussion

EPP curves in the absence and presence of chitosan are shown in Fig. 2 and the obtained data are given in Table 1. The inhibitor affected anodic reaction more than cathodic reaction, which suggests that the addition of inhibitor retards dissolution of metal. However, the difference in E_{corr} values reached 150 mV higher than in its absence suggesting that this inhibitor is predominantly anodic type. The highest efficiency obtained of 72% corroborate with values reported by other researchers for this polymer [9, 10]. The η_{IE} obtained for 800 ppm of chitosan was much higher than that obtained for 400 ppm, which may be related to a multilayer type of adsorption which leaves no part of the metal surface uncovered blocking all active sites.
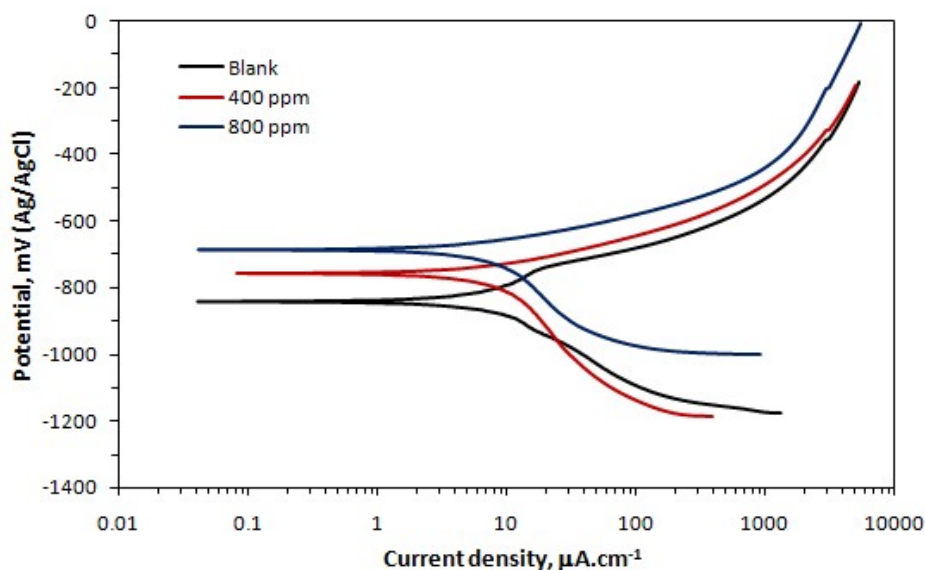

Figure 2 - Potentiodynamic polarization curves for mild steel in 0.1 M NaCl solution without and with two different concentrations of chitosan.

Table 1 – Potentiodynamic polarization parameters for mild steel in the absence and presence of chitosan.

Electrolyte	E_{corr} (mV vs Ag/AgCl)	i_{corr} ($\mu A.cm^{-2}$)	η_{IE} (%)
0.1 M NaCl	-840	6.1	---
0.1 M NaCl + 400 ppm chitosan	-760	3.4	44.3
0.1 M NaCl + 800 ppm chitosan	-690	1.8	72.1

Nyquist plots from EIS results are shown in Fig. 3. It is clear that Nyquist plots do not yield perfect semicircles as expected from the EIS theory. Depressed semicircles observed are often referred to the frequency dispersion of interfacial impedance as consequence of inhomogeneity of the electrode surface arising from its roughness or interfacial phenomena. The existence of a semicircle indicates the occurrence of a single charge transfer process during dissolution that is unaffected by the presence of the inhibitor [3].
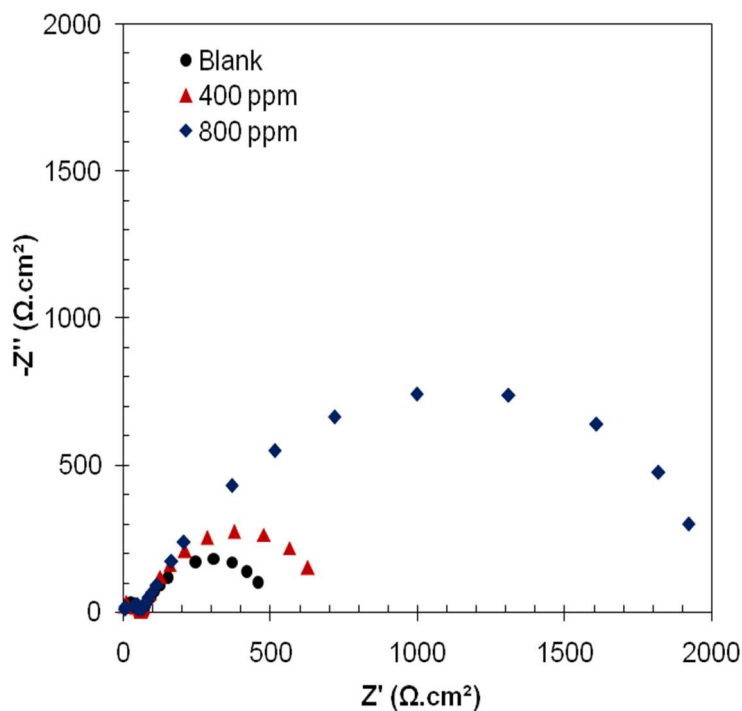

Figure 3 – Nyquist diagrams for mild steel in 0.1 M NaCl solution without and with two different concentrations of chitosan.

An equivalent circuit (Fig.4) was used to consider the processes involved in the electrochemical response of the system including R_s as resistance of the electrolyte, R_{ct} as a charge-transfer resistance and CPE as a constant-phase element. The CPE element was introduced to explain the depression of the semicircle due to surface heterogeneity. The impedance parameters were obtained by fitting the equivalent circuit and they are shown in Table 2. R_{ct} values increases with the concentration of chitosan, which indicates that this compounds is acting as an adsorption inhibitor forming a barrier for mass and charge transfer on the electrode surface. The variation in the η_{IE} values from EPP and EIS are acceptable due the inherent error related to the experimental method and fitting procedure.
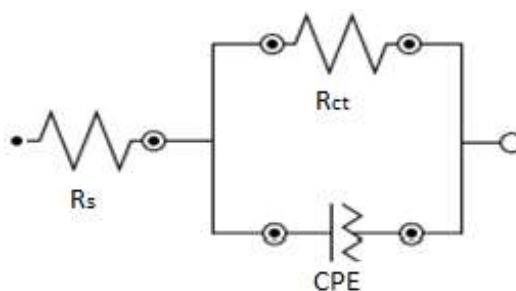

Figure 4 – Equivalent circuit.

Table 2 – Impedance parameters obtained from the equivalent circuit fitting.

Eletrolyte	R_s (Ω)	R_{ct} (Ω)	CPE (μF)	η_{IE} (%)
0.1 M NaCl	73	431	127	---
0.1 M NaCl + 400 ppm chitosan	68	632	103	31.8
0.1 M NaCl + 800 ppm chitosan	63	2093	349	79.4

Conclusions

Inhibitors play a vital role in providing protection against corrosion and there is a growing trend concerning green corrosion inhibitors for different metals in various aggressive environments. Chitosan is an important class of natural/bio-polymers that have several biological and industrial applications and it have been proved to be an eco-friendly corrosion inhibitor for mild steel in acid sodium chloride solution. The addition of chitosan to the blank solution is accompanied by a shift in E_{corr} to the noble direction with a more pronounced increasing in the inhibition efficiency with increasing concentration of the inhibitor. The presence of chitosan affected anodic reaction more than cathodic reaction, which suggests that the addition of this inhibitor retards dissolution of metal. Through EIS measurements it can be derived that chitosan behaved as an interface-type corrosion inhibitor that adsorbs at the metal/eletrolytic solution interface. It was shown that chitosan effectively hind carbon steel corrosion in acidic sodium chloride medium reaching inhibition efficiency above 70% for 800 ppm of the inhibitor.

Acknowledgements

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